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(54) Title: REINFORCEMENT MATERIAL

(57) Abstract

The invention relates to a reinforcement material, for instance for use in composites, comprising a first layer which at least consists of a plurality of substantially parallel filament bundles and at least one second layer which likewise consists of a plurality of substantially parallel filament bundles, which second layer lies at an angle relative to the first layer of between substantially 60° and 120°, preferably betwen 70° and 110°, more preferably between 80° and 100°, most preferably of 90°, wherein the first layer and the second layer are mutually adhered by means of an adhesive. The filament bundles are the weft threads of a woven fabric or web. The invention further relates to a method for manufacturing a reinforcement material.

REINFORCEMENT MATERIAL

The present invention relates to a reinforcement material, for instance for use as textile reinforcement in composites.

Composites can be strengthened using single or multi-layer structures, which structures can be manufactured from different materials. A much used type of reinforcement material is a woven fabric consisting of warp threads and weft threads. These form a right angle to each other. The warp threads therein lie in the 0° direction and the weft threads in the 90° direction. The composites made herewith are however an average of 70% less strong in the +45° and -45° direction. In order to solve this problem different techniques have already been proposed for making products which do strengthen in the +45° and -45° direction.

The European patent 0 193 497 describes for instance a woven fabric wherein the warp is a thermoplastic thread or a reinforcement thread coated with thermoplasts. After weaving the weft thread is displaced relative to the warp thread by means of a technique already per se known in the textile industry. The original right angle (90°) between warp and weft is hereby changed, usually into an angle of 45°. Two of these layers, one at an angle of +45° to the warp thread and one at an angle of -45° to the warp thread are subsequently laid on top of one another and then stitched together.

Another method is to manufacture webs from a number of parallel running threads or filament bundles, whereafter two such webs wherein the threads run in different directions are fixed to each other by means of knitting or stitching. This method is also per se known and can be performed using the multiaxial machines of the firms Liba and K. Mayer.

These known techniques have a number of drawbacks. Reinforcement layers which are stitched together have the drawback that the threads or filament bundles used are damaged by the stitching. At the points

where the stitching thread passes through a filament bundle an opening is created (so-called "resin pockets"). This also occurs when the bundles are knitted to each other. This phenomenon reduces the strength of the end product.

Figure 1 shows a reinforcement material manufactured using the above mentioned multiaxial knitting machine, in which the openings in the bundles are clearly visible. Shown in Figure 2 is a reinforcement material manufactured according to EP 0 193 497. Herein the resulting openings are even larger.

In addition, materials are often used for the fixing which are not compatible with the synthetic resin eventually to be used, such as thermoplastic stitching and knitting threads. This also has an adverse effect on the strength and durability of the material. The reinforcement threads are moreover not stretched.

It is the object of the present invention to obviate the above stated drawbacks.

This is achieved by the invention with a reinforcement material, for instance for use in composites, comprising a first layer which at least consists of a plurality of substantially parallel filament bundles and at least one second layer which likewise consists of a plurality of substantially parallel filament bundles, which second layer lies at an angle relative to the first layer of between substantially 60° and 120°, preferably between 70° and 110°, more preferably between 80° and 100°, most preferably of 90°, wherein the first layer and the second layer are mutually adhered by means of an adhesive.

The layers which are mutually fixed according to the invention by means of an adhesive can be webs or woven fabrics. In the case of webs the threads are preferably already placed beforehand in a direction differing from the length direction or warp direction at an angle of 30° to 60°, preferably at an angle of substantially 45°.

In the case of a woven fabric the weft thread will preferably be displaced relative to the warp direction after weaving.

Once the woven fabrics or webs have been brought into the suitable form, i.e. in a form wherein the weft threads or filament bundles lie in the desired direction, two or more layers are mutually fixed by means of an adhesive, such as for instance a thermoplastic or thermosetting powder or a glue. Instead of a powder another form of thermoplastic or thermosetting plastic can be used as long as the intended object, mutual adhesion of the layers, is achieved. Adhesion on the basis of a plastic is effected by heating and pressing together the entirety of the layers with the adhesive therebetween so that the plastic melts and both layers mutually adhere. The plastic used can be one on the basis of polyester, epoxy, acrylate and the like.

According to the present invention only a small quantity of powder is used. This is just sufficient to connect the layers in point-like manner to each other. In preference a maximum of 5% of the surface is thus mutually adhered. More than 95% of the contact surface of the two layers then remains free of powder. The reinforcement material is malleable and deformable. The biaxial reinforcement material is supplied to the user on rolls and can afterwards be impregnated with any thermosetting resin such as polyester, epoxy and phenol.

Alternatively, one or more of the layers can be sprayed or spread with a glue, for instance a water-dilutable dispersion, two-component glue etc., whereafter the two or more layers are pressed onto each other whereby they adhere.

The filament bundles and optional warp threads of which the layers according to the invention consist can be manufactured from any type of material known in the art, but glass fibre, carbon fibre, aramid fibre and the like are recommended.

Additional reinforcement materials can optionally be added together with the adhesive, such as for instance chopped threads of the above mentioned materials.

The present invention also relates to a method for manufacturing a reinforcement material, wherein the method comprises of:

a) manufacturing two or more layers, each at least consisting of a plurality of parallel filament bundles;

b) applying an adhesive to the first of the layers;

c) laying a second layer on the first layer;

d) optionally repeating the steps b) and c); and

e) causing the layers to adhere to each other.

The filament bundles are preferably stretched during adhering.

The reinforcement material obtained in this manner has a number of advantages. The reinforcement threads are preferably stretched completely flat and then chemically bonded to each other. The reinforcement material hereby has a high tensile strength, bending strength and elasticity modulus and flat composites with a high content of reinforcement material can be made. The width, angle and weight of the material can be varied as desired. In addition, heavier threads can be used whereby the material can be less expensive. The reinforcement thread is now not damaged by the stitching needle. Because the different layers are mutually adhered the reinforcement material can be punched, cut or otherwise processed without it fraying. The reinforcement material can thus be chopped into small strips.

In a preferred embodiment the adhesive powder has the same composition as the synthetic resin with which the composite is manufactured. The adhesive hereby forms an integral part of the end product. The advantage hereof is that no alien materials occur in the laminate,

which alien materials can often be the cause of the deterioration in mechanical properties due to capillary penetration of moisture or chemical products. Finally, there are no resin pockets in the composites which are made with the reinforcement material. Resin pockets are locations where there is no reinforcement. Such resin pockets can for instance occur when a prior art reinforcement material is used, whereby openings caused by the knitting or stitching needle are created in the filament bundle.

The present invention will be further elucidated with reference to the accompanying examples, which are only given by way of illustration and are not intended to limit the invention in any way.

EXAMPLES

EXAMPLE 1

A woven fabric was made with 3.5 glass fibres of 68 tex in the warp and 2.4 glass rovings (filament bundles) of 600 tex in the weft. By means of techniques per se known in this field, while stretching the weft threads these are then displaced relative to the warp threads such that an angle of 45° is formed between the two. A second woven fabric with the same composition is laid in reversed position onto the first woven fabric which has been sprayed beforehand with a thermoplastic powder. After heating and pressing together of the two layers there results a multiaxial, chemically bonded reinforcement material in 100% glass. Figure 3 shows a reinforcement material according to the invention to actual size. Figure 4 shows a detail. It is clearly visible that the used filament bundles and warp threads are not damaged. The material is well closed.

EXAMPLE 2

With the same materials as in example 1 but omitting the warp threads, a web is first made which is bound to a second web according to the same technique. In

this manner a biaxial chemically bonded reinforcement material is likewise manufactured.

EXAMPLE 3

The strength of a biaxial and triaxial reinforcement material according to the invention was determined in comparison to a known material.

3.1 Biaxial reinforcement material (+/- 45°)

A. Material 1 (according to the invention)

Composition:

0° direction contains 50 g/m² glass thread 68 Tex
+45° direction contains 200 g/m² "roving" of parallel threads of 600 Tex
-45° direction contains 200 g/m² "roving" of parallel threads of 600 Tex
90° direction contains no material

B. Material 2 (prior art, knitted to each other)

Composition:

0° direction contains no material
+45° direction contains 212 g/m² glass thread 136 Tex
-45° direction contains 212 g/m² glass thread 136 Tex
90° direction contains no material

The materials were applied as reinforcement material of a polyester laminate. Of this laminate the average bending strength in the 0°, +45°, -45° and 90° direction was determined in accordance with DIN 53452 with 50% by weight of glass. The average values of the four directions are shown in the following table:

Conditions	1 (N/mm²)	2 (N/mm²)	(1/2 x 100) - 100 (%)
dry	363	312	+16.3
after 4 hours boiling	339	298	+13.7

The average bending modulus was determined in the 0°, +45°, -45° and 90° direction in accordance with DIN 53457 with 50% by weight of glass. The average values of the four directions are shown in the following table:

Conditions	1 (N/mm^2)	2 (N/mm^2)	(1/2 x 100) - 100 (%)
dry	10771	10024	+ 7.4
after 4 hours boiling	10145	8641	+17.4

3.2. Triaxial reinforcement material

A. Material 1 (according to the invention)

Composition:

0° direction contains 400 g/m^2 "roving" of parallel threads of 600 Tex

+45° direction contains 200 g/m^2 "roving" of parallel threads of 600 Tex

-45° direction contains 200 g/m^2 "roving" of parallel threads of 600 Tex

90° direction contains no material

B. Material 2 (prior art, knitted to each other with polyester thread)

Composition

0° direction contains 400 g/m^2 glass thread 600 Tex

+45° direction contains 200 g/m^2 glass thread 320 Tex

-45° direction contains 200 g/m^2 glass thread 320 Tex

90° direction contains no material

The materials were applied as reinforcement material of a polyester laminate. Of this laminate the average bending strength in the 0°, +45°, -45° and 90° direction was determined in accordance with DIN 53452 with 50% by weight of glass. The results are shown in the following table:

Conditions	1 (N/mm^2)	2 (N/mm^2)	(1/2 x 100) - 100 (%)
dry	317	315	+0.6
after 4 hours boiling	280	213	+31.5

The average bending modulus was determined in 0°, +45°, -45° and 90° direction in accordance with DIN 53457 with 50% by weight of glass. The results are shown in the following table:

Conditions	1 (N/mm^2)	2 (N/mm^2)	(1/2 x 100) - 100 (%)
dry	9569	9569	+ 0
after 4 hours boiling	8852	6369	+39

In the above, Tex signifies: a thread of 1 km weighs 1 gram. The rovings were always of the same type and from the same manufacturer.

CLAIMS

1. Reinforcement material, for instance for use in composites, comprising a first layer which at least consists of a plurality of substantially parallel filament bundles and at least one second layer which likewise consists of a plurality of substantially parallel filament bundles, which second layer lies at an angle relative to the first layer of between substantially 60° and 120°, preferably between 70° and 110°, more preferably between 80° and 100°, most preferably of 90°, wherein the first layer and the second layer are mutually adhered by means of an adhesive.

2. Reinforcement material as claimed in claim 1, **characterized in that** the filament bundles are the weft threads of a woven fabric or web.

3. Reinforcement material as claimed in claim 1 or 2, **characterized in that** the filament bundles lie at an angle of 30° to 60°, preferably at an angle of substantially 45° relative to the length direction of the material respectively the warp threads of the woven fabric.

4. Reinforcement material as claimed in claim 1, 2 or 3, **characterized in that** the adhesive is a glue or a thermoplastic or thermosetting powder which is caused to melt with or without the influence of heat.

5. Reinforcement material as claimed in claim 4, **characterized in that** the glue is a water-dilutable dispersion or a two-component glue.

6. Reinforcement material as claimed in claim 4, **characterized in that** the powder is a polyester, epoxy, acrylate or other plastic or combinations thereof.

7. Reinforcement material as claimed in any of the claims 1-6, **characterized in that** the adhesive is mixed with an additional reinforcement component such as chopped fibres or the like.

8. Reinforcement material as claimed in any of the claims 1-7, **characterized in that** the filament

bundles consist of filaments chosen from the group consisting of glass fibres, carbon fibres, aramid fibres or combinations thereof.

9. Reinforcement material as claimed in any of the claims 1-8, **characterized in that** in addition to said first and second layers the material comprises one or more other reinforcement layers, chosen for instance from threads, rovings, mats, membranes, webs, woven fabrics, non-wovens and the like.

10. Reinforcement material as claimed in any of the claims 1-9, **characterized in that** the material and/or its constituent layers are pre-impregnated with a synthetic resin, chosen for instance from polyester, phenol, epoxy, polypropylene or combinations thereof.

11. Composites comprising at least one reinforcement material as claimed in any of the foregoing claims.

12. Method for manufacturing a reinforcement material as claimed in any of the claims 1-10, comprising the steps of:

a) manufacturing two or more layers, each at least consisting of a plurality of parallel filament bundles;

b) applying an adhesive to the first of the layers;

c) laying a second layer on the first layer;

d) optionally repeating the steps b) and c); and

e) causing the layers to adhere to each other.

13. Method as claimed in claim 12, **characterized in that** the filament bundles are the weft threads of a woven fabric.

14. Method as claimed in claim 12 or 13, **characterized in that** after or during manufacture of the layers of filament bundles the angle between the bundles and the length direction of the material respectively the warp threads of the woven fabric are changed such that it

amounts to 30° to 60°, preferably substantially 45° relative to the warp direction.

15. Method as claimed in any of the claims 12-14, **characterized in that** the adhesive is a glue and mutual adhesion of the bundles is brought about by pressing the layers onto each other.

16. Method as claimed in any of the claims 12-14, **characterized in that** the adhesive is a plastic powder and mutual adhesion of the bundles is brought about by heating the layers while they are pressed onto each other.

17. Method as claimed in any of the claims 12-16, **characterized in that** the filament bundles are stretched during the adhesion.

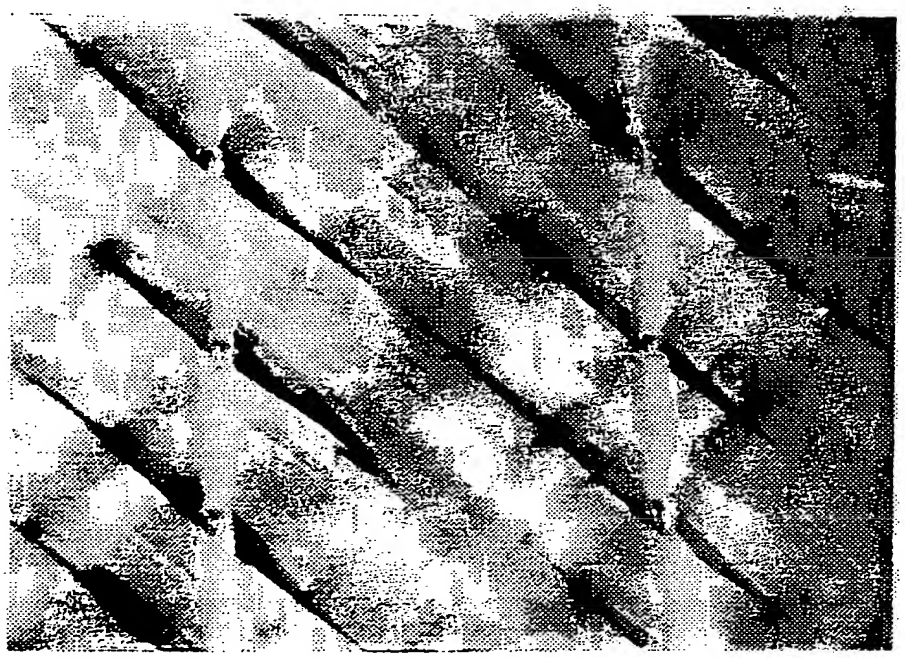

FIG. 1

FIG. 2

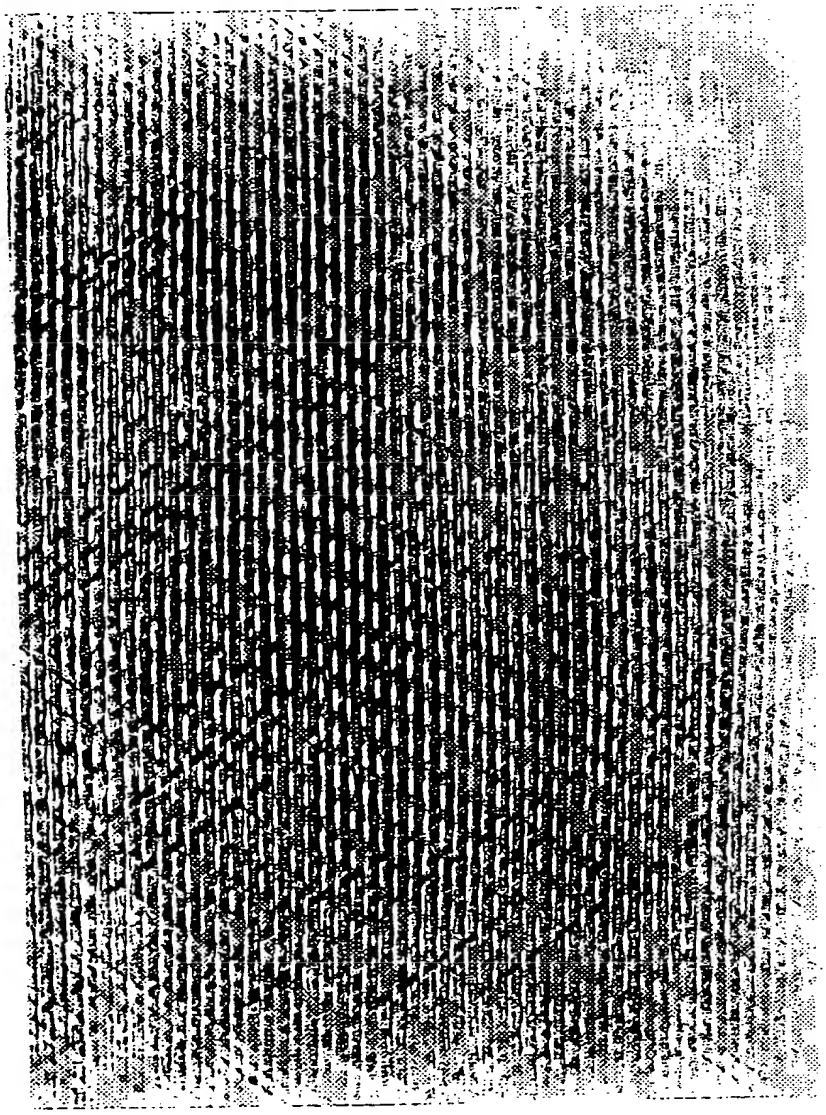

FIG. 3

FIG. 4

INTERNATIONAL SEARCH REPORT

Inte onal Application No
PCT/BE 97/00043

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B29C70/22 B29B15/14 B29C70/54

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B29C B29B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	EP 0 672 776 A (CHOMARAT & CIE) 20 September 1995 see the whole document ---	1-3,6,8, 9,11,12, 14,15,17
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X	EP 0 033 244 A (SMITH H R) 5 August 1981 see page 4, line 31 - page 6, line 30; figures 1-3A --- -/--	1,8,9, 11,12

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
12 June 1997	27. 06. 97

Name and mailing address of the ISA	Authorized officer
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Information on patent family members

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